

# Quantum spin fluctuations in the spin liquid state of $\text{Tb}_2\text{Ti}_2\text{O}_7$

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Neutron scattering experiments on a polycrystalline sample of the frustrated pyrochlore magnet  $\text{Tb}_2\text{Ti}_2\text{O}_7$ , which does not show any magnetic order down to 50 mK, have revealed that it shows condensation behavior below 0.4 K from a thermally fluctuating paramagnetic state to a spin-liquid ground-state with quantum spin fluctuations. Energy spectra change from quasielastic scattering to a continuum with a double-peak structure at energies of 0 and 0.8 K in the spin-liquid state. Specific heat shows an anomaly at the crossover temperature.

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## 1. Introduction

Magnetic systems with geometric frustration, a prototype of which is antiferromagnetically coupled Ising spins on a triangle, have been intensively studied experimentally and theoretically for decades [1, 2]. Spin systems on networks of triangles or tetrahedra, such as triangular [3], kagomé [4], spinel [5], and pyrochlore [1] lattices, play major roles in these studies. Their rich variety of phenomena includes zero temperature entropy in Ising antiferromagnets [3, 5] and in ferromagnetically coupled spin-ice [6], multiferroics induced by non-collinear magnetic structures [7], heavy fermion behavior [8], and unconventional anomalous Hall effect [9, 10].

Subjects that have fascinated many investigators in recent years are classical and quantum spin-liquid states [11–14], where conventional long-range order (LRO) is suppressed to very low temperatures. Quantum spin-liquids in particular have been challenging both theoretically and experimentally since the proposal of the resonating valence-bond state [11]. A prototype spin-liquid, or cooperative paramagnet, is the Heisenberg antiferromagnetic model on the pyrochlore lattice coupled by nearest-neighbor exchange interaction, which is shown to remain disordered at all temperatures [12]. The spin ice materials,  $\text{R}_2\text{T}_2\text{O}_7$  ( $\text{R} = \text{Dy}, \text{Ho}; \text{T} = \text{Ti}, \text{Sn}$ ), are the best-understood classical examples [15], while other experimental candidates found recently are awaiting further studies [13, 14].

Among magnetic pyrochlore oxides [1],  $\text{Tb}_2\text{Ti}_2\text{O}_7$  has attracted much attention because it does not show any magnetic LRO down to 50 mK and remains dynamic with short range correlations [16, 17]. Theoretical considerations of the crystal-field (CF) states of  $\text{Tb}^{3+}$  and exchange and dipolar interactions of the system [18–20] showed that it should undergo a transition into a mag-

netic LRO state at about  $T \sim 1.8$  K within a random phase approximation [20]. The dynamical ground state is a candidate for a quantum spin-liquid, but its puzzling origin has been in debate [1].

Recently, an interesting scenario to explain this spin-liquid state was theoretically proposed [21];  $\text{Tb}_2\text{Ti}_2\text{O}_7$  is a quantum-mechanical version of the classical spin-ice [6], where additional spin-flip terms to the otherwise classical Ising-spin Hamiltonian lift the macroscopic degeneracy of the classical “2-in, 2-out” ground states [21]. More recently a single-site mechanism was proposed [22] to account for the absence of LRO, in which the CF ground doublet becomes two singlets owing to a conjectured tetragonal distortion [23, 24], although this interpretation is not without difficulties [25].

In addition to the theoretical puzzle about the ground state, some experimental results of  $\text{Tb}_2\text{Ti}_2\text{O}_7$  contradict each other [16, 17, 26, 27]. It was concluded that the majority of the spins is dynamic down to 50 mK in [17]. On the other hand, in [26, 27] it was reported that about 50% of the spins are static at 0.4 K and that there is an unknown phase transition at 0.37 K. This discrepancy is probably caused by a certain uncontrollable parameter of crystalline samples. In fact, a recent study of specific heat showed a sample dependence for single crystals [24, 28]. However by restricting oneself to experimental data of polycrystalline samples, results are more consistent. Muon spin relaxation ( $\mu\text{SR}$ ) [16], neutron spin echo (NSE) [17], and susceptibility [29] experiments showed no conventional phase transition and LRO. Only a small amount ( $\sim 10\%$ ) of spins become quasi-static at 0.1–0.3 K [17, 29]. High-resolution neutron powder-diffraction experiments [30] showed that the crystal structure of  $\text{Tb}_2\text{Ti}_2\text{O}_7$  is consistent with the pyrochlore structure without disorder, Tb/Ti site interchange, or oxygen de-

ficiency.

In this work, we hypothesize that polycrystalline samples show the genuine characteristics of the spin-liquid state of  $\text{Tb}_2\text{Ti}_2\text{O}_7$ , and reinvestigate the low-temperature spin fluctuations of a polycrystalline sample by inelastic neutron scattering. From the NSE experiment [17], we expect that important spin fluctuations of the spin-liquid state should appear in the energy range  $E > 0.05$  meV, i.e., NSE time  $< 0.01$  ns (figure 3 of [17]), where no experimental data have been reported. The other aim of this work is to observe a certain temperature dependence of energy spectra around  $\sim 0.5$  K, anticipated from the quantum spin-ice theory [21]. In fact, the NSE [17] and our unpublished neutron scattering experiment [31] did suggest such a  $T$  dependence. We have found that around 0.4 K a high-temperature quasielastic spectrum becomes a continuum with a double-peak structure at energies of 0 and 0.8 K, indicating that a crossover from the paramagnetic to spin-liquid state occurs. Specific heat shows an anomaly at the crossover temperature.

## 2. Experiment

Polycrystalline samples of  $\text{Tb}_2\text{Ti}_2\text{O}_7$  were prepared by the standard solid-state reaction at 1350 °C from  $\text{Tb}_4\text{O}_7$  and  $\text{TiO}_2$  [16]. Most of the neutron-scattering measurements were performed on the triple-axis spectrometer NG5 at the NIST Center for Neutron Research. A sample with a weight of 7 g was mounted in a dilution refrigerator. The spectrometer was operated using a final neutron energy of  $E_f = 2.5$  meV, providing an energy resolution of 0.06 meV (full width at half maximum, FWHM) at the elastic position. Higher-order neutrons were removed by cooled Be and BeO filters. A few preliminary measurements were performed on the triple-axis spectrometer HER at the Japan Atomic Energy Agency [31]. Specific heat was measured by the heat-relaxation method on a physical-property measurement-system equipped with a  $^3\text{He}$  refrigerator.

## 3. Results and discussion

To investigate the ground state, we performed inelastic scattering experiments in a low energy range  $-0.1 \leq E \leq 0.5$  meV at low temperatures. In figures 1 and 2 we show constant- $Q$  scans measured at several wave vectors in a range  $0.6 \leq Q \leq 1.6 \text{ \AA}^{-1}$ . Since the first excited CF level is about 18 K or 1.7 meV [16, 32], the  $E$  spectra of these figures are transitions among the ground doublet of the CF states of  $\text{Tb}^{3+}$ , being in the trigonal symmetry [18]. The typical energy scale of these  $E$  spectra is the order of 0.1 meV  $\sim 1$  K. This value agrees well with the estimate of the effective Tb-Tb spin exchange-interaction based on  $\mu\text{SR}$  [16, 18]. Thus the observed  $E$  spectra represent spin fluctuations of up and down states of the  $\text{Tb}^{3+}$  Ising-like spins [18], interacting via the inter-site couplings and virtual excitations to the excited doublet [19–21].

One can see from figure 1 that the  $E$  spectra change remarkably between  $T = 1.5$  and 0.1 K from a quasi-elastic

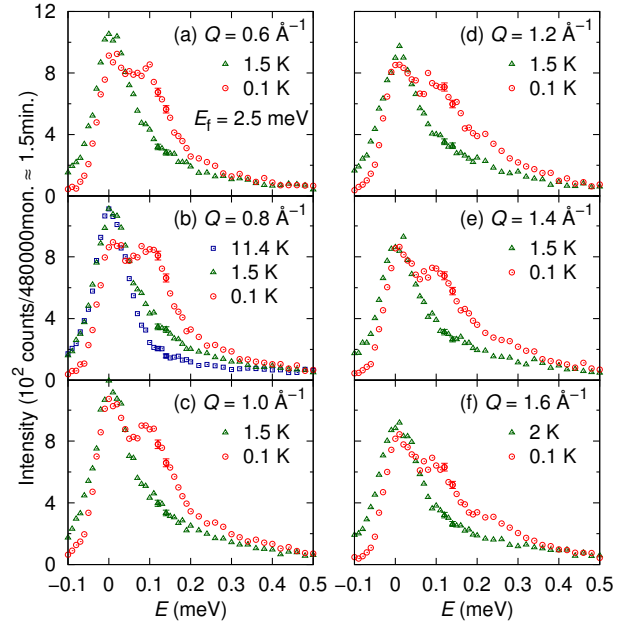


FIG. 1. Constant- $Q$  scans taken at  $Q = 0.6, 0.8, 1.0, 1.2, 1.4, 1.6 \text{ \AA}^{-1}$  in the energy range  $-0.1 \leq E \leq 0.5$  meV measured at temperatures above and below 0.4 K.

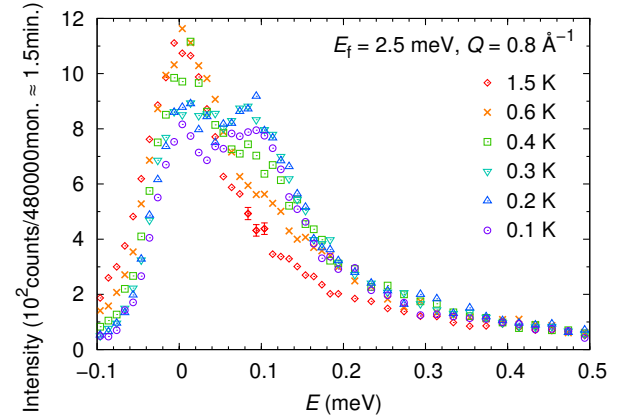


FIG. 2. Constant- $Q$  scans at  $Q = 0.8 \text{ \AA}^{-1}$  in an energy range  $-0.1 \leq E \leq 0.5$  meV measured at several temperatures down to 0.1 K.

scattering centered at  $E = 0$  to an inelastic scattering with an additional peaked structure at  $E \simeq 0.1$  meV. Temperature dependence shown in figure 2 indicates that the spectral change occurs around  $T = 0.4$  K. We think that this crossover has an important implication that the paramagnetic states above and below 0.4 K have very different characteristics. The  $E$  spectra (figure 2) become a low- $T$  limit only below 0.3 K, and we may conclude that  $\text{Tb}_2\text{Ti}_2\text{O}_7$  condenses into the spin-liquid ground-state below this temperature. It should be noted that in the same crossover  $T$  range a significant change was

observed in the NSE spectra (figure 3 of [17]). In contrast to this inelastic scattering, the energy-integrated diffraction varies only slightly below 1.5 down to 0.05 K (figure 2 of [17]), i.e., spin correlations over a single tetrahedron are retained at low temperatures [16].

The  $E$  spectra in figure 1 above 0.2 meV at 0.1 K exhibit additional  $Q$ -dependent structures. This  $Q$ -dependence seems to impose a restriction on the origin of the spin-liquid ground-state; it is brought about by a many-body effect [18–20]. An interesting proposal along this line is the quantum spin-ice state, where a singlet ground state is formed predominantly from the “2-in, 2-out” classical spin-ice states within a single tetrahedron [21]. The estimate of an energy band spanned by excited states is the order 0.5 K [21]. This value approximately agrees with the fit parameter  $\Delta$  of the inelastic Lorentzian function at  $T \leq 0.3$  K, which is discussed later.

Quite recently another possibility of the spin-liquid state considering both single- and inter-site effects has been pointed out [22]. The authors hypothesize that the ground doublet in the cubic pyrochlore structure splits into two singlets under a small tetragonal distortion, conjectured to exist as high as 1.6 K [22]. The energy splitting of 0.19 meV between the two singlets, which is claimed [22] to be observed at 1.6 K in a neutron inelastic spectrum in [32], is not reproducible in the present data of figures 1 and 2 at 1.5 K. The energy resolution 0.16 meV (FWHM) in [32] seems too large to exclude an artifact in a resolution-convolution fitting. Thus the theoretical two-singlet scenario [22] assuming the tetragonal distortion would be seriously modified to account for the present  $E$ -spectra and  $T$ -dependence, in which the crossover around 0.4 K could perhaps be ascribed to a structural transition.

In order to parameterize the  $E$  spectra shown in figure 2 as a function of temperature, we carried out fits of the data to a scattering function

$$S(Q, E) = A\delta(E) + \frac{B}{1 - e^{-E/k_B T}} \sum_{\pm} \frac{\Gamma E}{(E \pm \Delta)^2 + \Gamma^2}, \quad (1)$$

which is convoluted with a resolution function. The first and second terms of equation (1) represent elastic and inelastic scatterings, respectively. Typical results of the fitting are shown in figure 3. For data at 1.5 K we tried to fit the spectrum using the Lorentzian function ( $\Delta = 0$ ) for standard quasielastic scattering with ( $A \neq 0$ , figure 3(a)) and without ( $A = 0$ , figure 3(b)) the elastic component. These fits show that the elastic component, 20~30% of the energy integrated ( $E < 0.5$  meV) total intensity, cannot be neglected in this analysis. The elastic part consists of incoherent elastic scattering of Ti nuclei, multiple Bragg scattering, and magnetic scattering of  $\text{Tb}^{3+}$  spins [17]. In the present experiment, the separation of the elastic scattering from the inelastic scattering is difficult

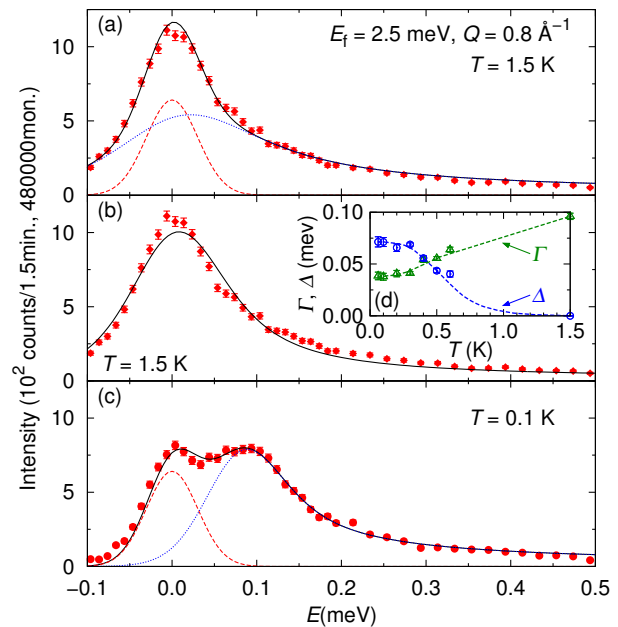


FIG. 3. Results of fitting constant- $Q$  scan data at  $T = 1.5$  K (a,b) and 0.1 K (c) shown in figure 2 to resolution convoluted  $S(Q, E)$  of equation (1). We assume (a)  $\Delta = 0$ , and (b)  $A = 0$  and  $\Delta = 0$ . Red dashed-lines and blue dotted-lines represent the resolution convolutions of the elastic and inelastic scattering of equation (1). The black solid-lines are total fitted curves. (d) Temperature dependence of the fit parameters  $\Gamma$  and  $\Delta$ . Lines are guides to the eye.

owing to the insufficient instrumental energy-resolution compared to the energy scale of 0.1 meV. We could not obtain a reasonable  $T$ -dependence of the parameter  $A$  of equation (1), and assumed the same  $A$  value for all temperatures. Resulting fits are shown in figures 3(a) and (c).

The temperature dependence of the fit parameters  $\Gamma$  and  $\Delta$  are plotted in figure 3(d). These parameters show the crossover behavior around 0.4 K. At 0.1 K the second term of equation (1) with  $\Delta \sim 2\Gamma$  represents a quasi-gapped continuum with a significant spectral weight at  $E = 0$ . It should be noted that the very high resolution NSE data [17] imply that  $\sim 20\%$  of the elastic component in equation (1) contains a magnetic contribution below 0.3 K. Thus the magnetic spectrum, background subtracted equation (1), in the spin-liquid state probably has a two-peak structure at  $E = 0$  and 0.07 meV. This should be confirmed more directly using another spectrometer with a much higher resolution  $\sim 10 \mu\text{eV}$  or better in further work.

We measured the specific heat  $C_P$  of the polycrystalline sample to check whether the crossover around 0.4 K can be observed in thermodynamic properties. The result is plotted in figure 4 together with previous measurements.  $C_P$  of the present work shows an upturn below 0.5 K,

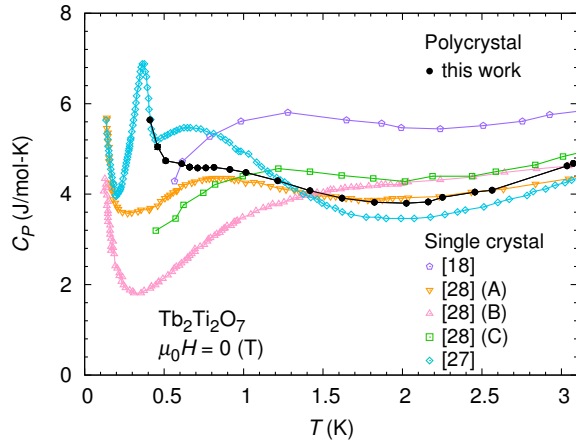


FIG. 4. Temperature dependence of specific heat of polycrystalline and single-crystalline samples [18, 27, 28].

being consistent with the neutron data. We checked that the same upturn of  $C_P$  is observed by a polycrystalline sample prepared in the same way as described in [16, 17]. One can also see differences of  $C_P$  for crystalline samples [18, 24, 27, 28], demonstrating the difficulty of discussing experimental data taken on different single crystals, especially below 1 K. Control parameters of single crystals could be very small disorders, Tb/Ti site interchange, oxygen deficiency, or local stress built-in during single-crystal growth carried out using image furnaces. We speculate that the large differences of  $C_P$  at low  $T$  may imply that the system is located close to a quantum critical point which is affected by these hidden material parameters. We hope that the mechanism of the spin-liquid state can be explored further in studies on well-characterized single crystals.

#### 4. Conclusion

In summary, inelastic neutron scattering has been used to extend the work of [16, 17] and explore the spin-liquid state of polycrystalline  $\text{Tb}_2\text{Ti}_2\text{O}_7$ . This system condenses into a quantum spin-liquid state from the paramagnetic state via a crossover around 0.4 K, where specific heat shows an anomaly. The energy spectrum in the spin-liquid state is a continuum with a double-peak structure at energies of 0 and 0.8 K. Its wave-vector dependence suggests that the spin-liquid state is brought about by many-body effects [18, 21].

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